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An Investigation of some

[illegible]

Dissertation

submitted to the Board of University
Studies of the Johns Hopkins Uni-
versity for the degree of Doctor of Philoso-
phy by

[illegible]

71837

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[illegible]:
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Cresols [illegible]
Resorcinol [illegible]
Hydroquinone [illegible]
Pyrogallol [illegible]
Amidophenols [illegible]
[illegible] [illegible]
[illegible] [illegible]
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An Investigation of some Derivatives of Orthosulphobenzoic acid.

The many cases in the literature of the derivatives of orthosulphobenzoic acid prepared from the two isomeric chlorides of this acid, have shown many anomalies, and not less striking differences to the behavior of phthalic acid derivatives under similar conditions. It remains, therefore, of interest to ascertain how the anhydride of ortho-sulpho-benzoic acid would conduct itself towards ammonia. To investigate this the present work was undertaken at the suggestion of Professor Remsen.

The anhydride of orthosulphobenzoic acid was prepared by Fahlberg and

Hugo[1] by the action of acetyl chloride on the free acid, also by the action of phosphorus pentachloride on the ammonium potassium salt the resulting anhydride as a solid [illegible] at 70°. They described it as ~~crystallizing~~ in monoclinic [illegible] system, with melting-point at 71°. They studied the action of water upon it. About the same time Remsen and [illegible][2] obtained it by heating a mixture of the acid and phosphorus pentoxide at 130°, as a sublimate in fine needles melting at 128°.

Oscar Weber[3] by the action of acetyl chloride on metasulphoparatoluic acid, derived from methylsaccharin, obtained the anhydride and studied the action of ammonia

1 Ber. XXII 754

2 Am. Chem. J. XI 331

3 Ber. XXV 1739

upon it.

The anhydrides of benzoic ortho-sulpho-benzoic acid has been obtained by two workers in this laboratory.

Preparation of Material.

The material used for the preparation of the anhydride, in this work, was the acid potassium salt of ortho-sulpho-benzoic acid obtained from commercial saccharine containing about 60 per cent benzoic sulphinide by substantially the same method as described by Remsen and Saunders.+

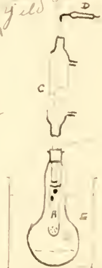
The difficulties in handling and preserving the solutions in anhydrous ether and benzene led to the rejection of the methods of Fahlberg and of Weber. Sublimation did not yield the anhydride in sufficient quantity. Moreover the crystals

+ Am. Chem. J. 17–347

the [illegible] free [illegible] decomposes much more promptly than the [illegible] hydrogen [illegible] by the [illegible]

The [illegible] [illegible] of [illegible] acid potassium [illegible] (about 25 grams) is intimately mixed in a mortar with the equivalent amount (22 grams) of phosphorus pentachloride. The temperature at which the action begins varies with the purity of the chemicals; with pure, dry reagents it is sufficient to some extent, but the presence of small amounts of phosphorus oxychloride considerably affects this. After the evolution of hydrochloric acid has ceased the mass is heated for some time to decompose any [illegible] formed and to expel some of the oxychloride of phosphorus. On cooling, the mass is granulated roughly

and placed in a continuous extractor and the separation effected by ~~the~~ anhydrous benzene. The concentrated solution in the extractor was allowed to cool slowly and deposited clear, colorless crystals, from ten to fifteen millimeters in length, they were practically pure. The benzene employed must be pure or dark ~~[illegible]~~, tarry products are obtained — an ethereal solution of the anhydride with some thiophene deposited a black mass on exposure to the light. The presence of phosphorus oxychloride in the solution seems to favor the formation of [illegible] [illegible]. The yield is [illegible] yield of [illegible]



The apparatus, represented in the figure, was found to work very efficiently. A test tube [illegible] x [illegible] mm. was sealed [illegible] numerous [illegible]-sized holes made

by heated potassium [illegible], the [illegible] of which consisted in [illegible] chloride [illegible]. A hot water-bath was used. A rubber stopper was used ~~to~~ in the mouth of the flask.

The reaction between the salt and pentachloride may be expressed:

$$C_6H_4{<}^{CO\cdot OH}_{SO_2OK} + PCl_5 = C_6H_4{<}^{CO}_{SO_2}{>}O + POCl_3 + KCl + HCl$$

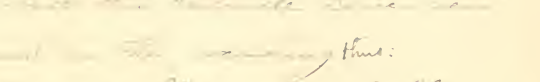
Limpricht und Uslar[5], have received [illegible] monochloride of the metasulphobenzoic acid [illegible] [illegible] in this laboratory has prepared the [illegible] compound [illegible] [illegible]. It was [illegible]

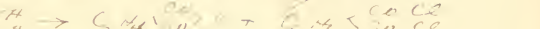
5 — [illegible]

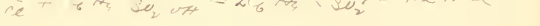
a compound might be formed with the other acid hydroxyl group with formation of sulphonyl

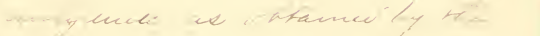
$C_6H_4 < ^{OH}_{SO_2 \cdot OH} \rightarrow C_6H_4 < ^{OH}_{SO_2Cl} \rightarrow C_6H_4 < ^{Cl}_{SO_2Cl}$

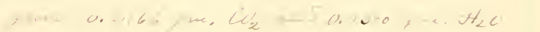
[illegible] mixture with pentachloride was brought first to a low temperature and the resulting mass poured into cold water. A milky flocculent precipitate separated which was washed with cold water free from [illegible] [illegible] and dried between filter-papers. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] chlorine and the [illegible] [illegible] [illegible]. The chlorine content was minute and no [illegible] [illegible] than could be obtained. But, in the action of phosphorus penta-chloride in sufficient proportion at low temperatures [illegible] [illegible] the formation of the [illegible] [illegible] [illegible]

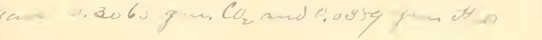












IV 0.2012 grm. gave [illegible] grm. $BaSO_4$ ([illegible])

	$C_7H_4O_4S$	I	II	III	IV
C	45.64	[illegible]	[illegible]	[illegible]	—
H	2.17	2.36	[illegible]	[illegible]	—
S	17.39	—	—	—	[illegible]

The [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]. Analysis I was made by Mr. [illegible] of this University.

The anhydride of ortho-sulpho-benzoic acid is thus [illegible] [illegible] [illegible] [illegible] [illegible] crystals. It also [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] of ortho-sulpho-benzoic acid. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]. S [illegible] [illegible]

Action with Alcohols

Alcohols dissolve the anhydride with the formation of acid esters of orthosulpho[illegible] i.e. acids:

$$C_6H_4<^{CO}_{SO_2}>O + ROH = C_6H_4<^{CO.OR}_{SO_2.OH}$$

Similar action was observed by Remsen and [illegible] by the action of alcohols on the chlorides; They ascribed the formula above given, on account of the general properties and the ability to form [illegible] esters.

<u>Methyl alcohol</u>. — When the anhydride is treated with methyl alcohol (absolute or 98%) it dissolves with evolution of heat. On evaporating the resulting solution, a thick syrup was obtained, which [illegible] crystallised on standing, [illegible] deliquescent [illegible]. [illegible] must be [illegible].

$C_6H_4 \begin{matrix} CO \\ SO_2 \end{matrix} O + CH_3OH - C_6H_4 < \begin{matrix} CO \cdot CH_3 \\ SO_2 \cdot OH \end{matrix}$.

[illegible] by Bunsen and Kolbe and by Kuslake[6].

The Silver salt, $C_6H_4 < \begin{matrix} CO \cdot CH_3 \\ SO_2 \cdot OAg \end{matrix}$, was obtained by dissolving silver carbonate in the alcoholic solution of the ester. It crystallized from concentrated solutions in plates. The solution [illegible] considerably in the [illegible] on exposure of the crystals.

0.2005 gm. gave 0.0665 gm. Ag = 33.6 %

The above formula requires 33.4 % Ag

The Potassium salt, $C_6H_4 \begin{matrix} CO \cdot OCH_3 \\ SO_2 \cdot OK \end{matrix}$, was similar to that [illegible] Kolbe.

0.[illegible] gm. gave 0.142 gm. $BaSO_4$ (Kubly method)

0.[illegible]30 gm. gave 0.0562 gm. K_2SO_4

	formula	found
S	1[illegible].59	1[illegible].51
K	1[illegible]	1[illegible].0

6 — Dissertation J.H.U. 1895

Ethyl alcohol [illegible] the [illegible]
[illegible] the [illegible] [illegible]
[illegible] group like the corresponding methyl
derivative showing signs of [illegible]
The Potassium salt, $C_6H_4 < {}^{C_2H_5O}_{SO_2OK}$, crystal-
lized in pearly plates, and [illegible] very soluble.

0.2[illegible] gm. gave 0.[illegible] gm. K_2SO_4 = 14.48
percent potassium. The [illegible] required [illegible]
percent.

The Silver salt, $C_6H_4 < {}^{C_2H_5O}_{SO_2Ag}$, crystallized
in deliquescent needles.

0.243 gm. gave 0.1375 gm. Ag = 31.76 per
cent silver. The theory requires [illegible] per cent Ag

Action with Phenols

By the action of phenols with the anhydride [illegible] sulphonphthaleins are obtained [illegible] plain [illegible] [illegible] [illegible]. Some of these substances, especially [illegible] [illegible] [illegible] have been extensively studied in this laboratory[7]. White[8] using the acid with phenols in [illegible] presence of dehydrating agents obtained colored products [illegible] [illegible] [illegible] [illegible] conditions. Under the conditions employed by him, the anhydride must have been present, and the [illegible] [illegible] [illegible] [illegible] cannot be attributed to the [illegible] employed. The sulphonphthaleins, [illegible] [illegible] [illegible] [illegible] [illegible] conditions [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible],

7 – [illegible]

8 – [illegible]

to a little amount of the resulting [illegible] cause of decomposition, the time is considerable.

An attempt was made to [illegible] condensation [illegible] in the presence of heating solutions of the anhydride and phenols with dehydrating agents. Only with resorcinol after several days was a slight color observed. When the anhydride and phenol (or cresol) are mixed, a bright red color is seen but the reaction does not seem to continue.

The filtrates from the phenolsulphonphthaleins were examined, but no evidence could be found of the formation of benzoyl benzoic sulphonic acids. The reaction taking place as represented:

$$C_6H_4<{CO \atop SO_2}>O + 2HRH = C_6H_4<{CR_2 \atop SO_2}>O$$

The mother substance sulphonphthalide $C_6H_4<{CH_2 \atop SO_2}>O$ was prepared by Holmes[9] by

9- Am. Chem. Jour. [illegible]

the action of hydrogen sulphide on the [illegible] chlorides.

The sulphur compounds [illegible] are [illegible] substances more soluble than the corresponding compounds of platinic acid. They are soluble in [illegible] from which they are precipitated by water.

During the [illegible] not neutralize the product but the amount of [illegible] yield were thus changed.

Phenol sulphonic acid [illegible]

[illegible]

[illegible] soluble [illegible]

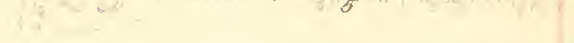
[illegible]

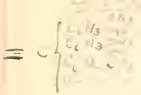
[illegible] gave up [illegible]

An effort was made

in solution.

In order to obtain a satisfactory triphenylmethane-sulphonic acid, the sulphon-phthalein was boiled for fifty hours with concentrated hydrochloric acid, but no ~~sign~~ indication of decomposition was noticed [illegible]. [illegible] With [illegible] decomposition [illegible] [illegible] from the [illegible] [illegible] [illegible] [illegible]





	$C_{19}H_{12}BO_6$
C	61.9%
H	3.2%
B	5.9%

The 1st [illegible] [illegible] [illegible] [illegible] 0.2003 [illegible]

gm. but 0.1[illegible] gm. [illegible] the [illegible] gave 0.0868 gm. $BaSO_4$ corresponding to 5.82 per cent sulphur. [illegible]

The [illegible] sulphide was [illegible] in the [illegible]

Hydroquinol sulphonphthalein.—Hydroquinol reacts more slowly than resorcinol, the mass as obtained by precipitating the alkaline solution by acid was a dark brown [illegible], exceedingly difficult to filter. It is less soluble than the sulphonfluorescein, the alkaline solution being [illegible] and not fluorescent.

I. .1930 gm. gave 1.1135 gm. $BaSO_4$ = [illegible] per cent sulphur.

II. [illegible] gm. gave [illegible] gm. $BaSO_4$ = [illegible] per cent sulphur.

Action with Ammonia.

The action of ammonia upon the anhydride of o-sulphobenzoic acid has been studied by Fahlberg and Barge, and verified in the present work. When studying the action of ammonia on the anhydride of metasulphobenzoic acid. In each case the reaction was the formation of the ammonium salt of a benzamide sulphonic acid in accordance with the equation

$$C_6H_4 <^{CO}_{SO_2}> O + 2NH_3 = C_6H_4 <^{CONH_2}_{SO_3NH_4}$$

The anhydride was dissolved in anhydrous ether (or chloroform), and dry ammonia gas passed into the solution ~~treated~~ with continual stirring until the ether was saturated. A white crystalline precipitate was formed. This was filtered off, and

$C_7H_{10}SN_2O_5$ [illegible]		I	II	III	IV	V
N	[illegible]	12.07	—	—	—	—
N (as NH_2)	[illegible]	—	6.39	—	—	—
S	[illegible]	—	—	14.70	14.75	14.65

Analysis V was made by Mr. E. E. Reid of this laboratory.

<u>Barium</u> <u>ortho benzamide sulphonate</u>

$(C_6H_4<^{CONH_2}_{SO_2O})_2Ba\cdot5H_2O$. — This salt ~~[illegible]~~ is very soluble in water. The solution evaporates only to a thick syrup, not readily crystallizing. From dilute alcohol it crystallizes in white tufts of little needles. [illegible] is described by [illegible] prepared from ortho [illegible] sulphobenzoic acid.

Of the crystals

0.3[illegible] gm. lost [illegible] gm. [illegible]

[illegible]

[illegible]

II [illegible] gm. lost [illegible] gm. at [illegible] and

gave [illegible] gm. [illegible]

	[illegible]	I	II
[illegible]	[illegible]	[illegible]	[illegible]
H_2O	[illegible]	[illegible]	[illegible]

Potassium [illegible] benzamine sulphonate,

$C_6H_4 \begin{matrix} CO \cdot NH_2 \\ SO_2OK \cdot H_2O \end{matrix}$, crystallized from [illegible] alcohol in small needles easily soluble in water:

Of the crystals.

I [illegible] gm. lost [illegible] gm. at 140 and gave

0.0754 gm. K_2SO_4

II [illegible] gm. lost 0.0129 gm. at 140 and gave

[illegible] gm. K_2SO_4.

	Estimated	I	II
H_2O	7.00	6.[illegible]	7.11
K	15.21	15.22	[illegible]

The potassium [illegible] was [illegible]

Action with Aromatic Amines.

condition

It was

[illegible] at

[illegible]

[illegible]. I [illegible]

[illegible]. Thus, [illegible] it,

[illegible] of [illegible]. The

two substances obtained appear, therefore, to be

[illegible]

[illegible]

[illegible]

$C_6H_4 \cdot CO_2 \cdot OK \cdot C_6H_5 \rightarrow C_6H_4 \cdot CO_2 \cdot NC_6H_5 \rightarrow C_6H_4 \cdot CO_2 \cdot OH \cdot NC_6H_5$

Equivalent quantities of the [illegible]

[illegible]

[illegible]. The [illegible]

[illegible]

was obtained

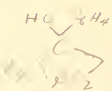
[illegible]

[illegible]

I [illegible]

[illegible] its melting-point was

[illegible]



Action with Aldehydes.

appear, therefore, to be that

[illegible]

[illegible] B [illegible]

Action with Monosaccharides.

Attempts were made to [illegible] [illegible] in presence of [illegible]

Action with Phosphorus pentachloride

Phosphorus pentachloride acting on the [illegible] prepared with [illegible] of [illegible] [illegible]. The action varied very much according to the [illegible] the purity of the chemicals, temperature and time of action. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] of [illegible] [illegible] [illegible]. At 20° no action took place, even though the mass was liquefied with phosphorus pentachloride. It was concluded from numerous experiments that the formation of the [illegible] chloride was favored by high temperatures [illegible] [illegible] [illegible]. [illegible] [illegible] [illegible] [illegible] [illegible]

Conclusion

Biographical

The author was born in Washington, D.C. [illegible] 18[illegible]. His preparatory education was in the public schools of that city. On graduating from the High School (18[illegible]) he entered the Chemical Department of Lehigh University, and [illegible] the degree of Analytical Chemist in 1891. He [illegible] the degree of [illegible] in 189[illegible].

After graduating, he was assistant chemist at the [illegible] ([illegible]); subsequently [illegible] the [illegible] Mass. Inst. of Technology, and then, during the collegiate years 1891-4, was instructor in chemistry at Lehigh University. In 1892 he was assistant in the laboratory of the U.S. [illegible] at Washington D.C.

He entered the Johns Hopkins University in 1879 and then followed courses in Chemistry, Biology and Physics, and was appointed Laboratory Assistant during the present year.